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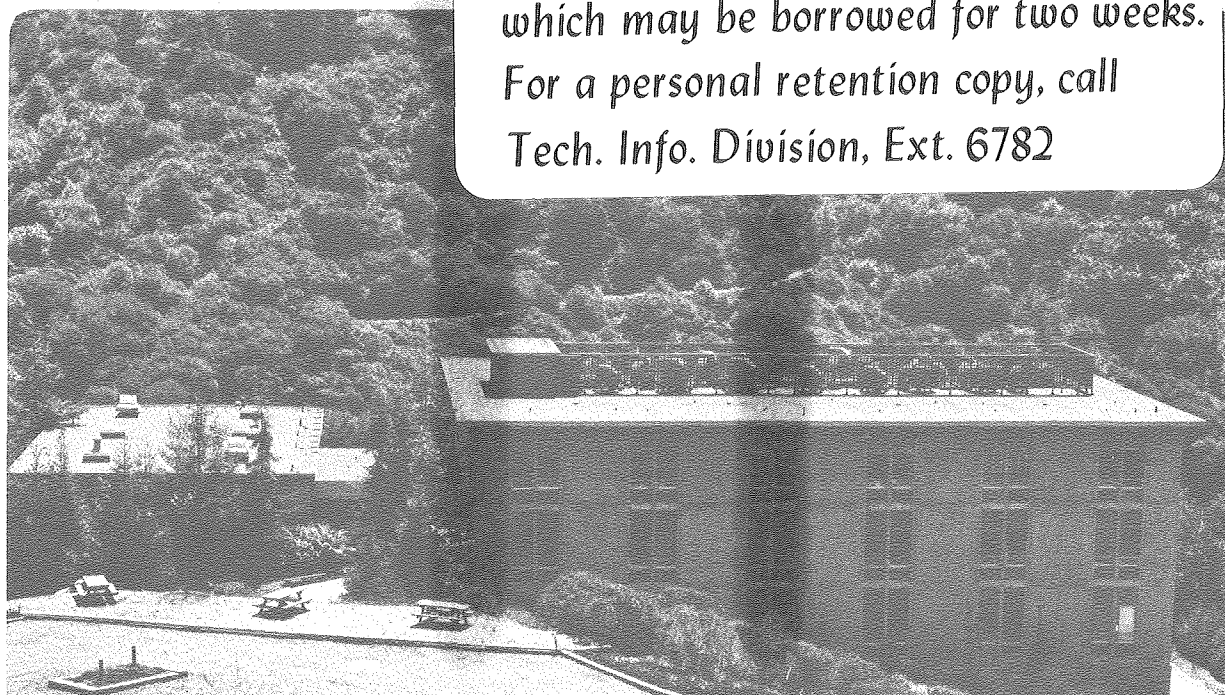
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MIXTURES: APPLICATION OF THE LOCAL-COMPOSITION  
CONCEPT

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EQUATIONS OF STATE FOR STRONGLY NONIDEAL FLUID MIXTURES:  
Application of the Local-Composition Concept

Wallace B. Whiting and John M. Prausnitz

Lawrence Berkeley Laboratory and  
Department of Chemical Engineering  
University of California  
Berkeley, California 94720

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## ABSTRACT

A new model has been developed for calculation of fluid-phase equilibria of asymmetric mixtures. This local-composition model extends the quasi-chemical theory of Guggenheim (known to correlate well liquid-state activity coefficients) to fluids of all densities. The model can be applied to any equation of state, contains only one new adjustable parameter per binary pair, and can be extended to multicomponent mixtures of large and small molecules by use of the surface areas of the molecules. Although the local-composition model is a nonrandomness approach, all randomness boundary conditions are met. Significant improvement over the random-mixing model is shown for the prediction of vapor-liquid equilibria of methane/water and ethane/water systems.

## INTRODUCTION

New equations of state for pure fluids appear frequently in the technical literature. New ways to apply these equations to mixtures, however, appear only seldom, even though it is well known that an equation of state that correlates well the thermodynamic properties for each of two pure fluids does not necessarily predict well the vapor-liquid equilibria for the binary mixture. Several sets of mixing rules for pure-component parameters have been proposed, but nearly all

involve the random-mixing assumption--a serious flaw. Most of these mixing rules are only slight perturbations of those of van der Waals (1890), who first suggested the one-fluid mixture model.

In this work, we propose a significantly different procedure for extending an equation of state to mixtures; our primary concern is to take nonrandomness into account. Although nonrandomness theories for liquid mixtures are not new, few studies apply these theories to the prediction of both vapor and liquid properties. Starting from the two-fluid approach (which underlies the Wilson [1964], NRTL [Renon and Prausnitz, 1968], UNIQUAC [Abrams and Prausnitz, 1975], and other liquid-state activity-coefficient models), we have developed a consistent mixture theory for fluids at all fluid densities. Our local-composition theory is based on reasonable approximations for the degree of nonrandomness in a fluid mixture and meets the close-packed liquid and ideal-gas limits.

In this paper, we explain the underlying principles of our model, give examples of how it differs from random-mixing models, and show how to apply it to any equation of state of the van der Waals form (e.g., equations such as Redlich-Kwong [1949], Peng-Robinson [1976], and Soave [1972]).

## ONE-FLUID THEORIES

Extension of pure-fluid equations of state to mixtures was first proposed by van der Waals (1890). For the two

pure-component parameters in his equation of state, he suggested, based on physical arguments, the following well-known mixing rules:

$$a = \sum_{i=1}^m \sum_{j=1}^m x_i x_j a_{ij} \quad (1)$$

$$b = \sum_{i=1}^m \sum_{j=1}^m x_i x_j b_{ij} \quad (2)$$

Berthelot (1898) and Lorentz (1881) suggested that the following expressions be used for the  $ij$  parameters:

$$a_{ij} = \sqrt{a_{ii} a_{jj}} \quad (3)$$

$$b_{ij} = (b_{ii} + b_{jj})/2 \quad (4)$$

This set of mixing rules (Equations 1-4) is equivalent to the "molecular" mixing rules

$$\epsilon \sigma^3 = \sum_{i=1}^m \sum_{j=1}^m x_i x_j \epsilon_{ij} \sigma_{ij}^3 \quad (5)$$

$$\sigma^3 = \sum_{i=1}^m \sum_{j=1}^m x_i x_j \sigma_{ij}^3 \quad (6)$$

$$\epsilon_{ij} = \sqrt{\epsilon_{ii} \epsilon_{jj}} \sqrt{\sigma_{ii}^3 \sigma_{jj}^3} / \sigma_{ij}^3 \quad (7)$$

$$\sigma_{ij} = (\sigma_{ii}^3 + \sigma_{jj}^3)/2 \quad (8)$$

where  $\epsilon$  is the minimum potential energy and  $\sigma$  is the collision diameter of some simple, though arbitrary, two-body intermolecular-potential function. Equation 6 was verified as a reasonable approximation by Henderson and Leonard (1970),

based on computer simulations of mixtures of hard-sphere molecules; however, Equation 8 should be replaced by

$$\sigma_{ij} = (\sigma_{ii} + \sigma_{jj})/2 \quad . \quad (9)$$

Likewise, Equation 5 is a reasonable approximation, based on the first term of the perturbation series for the Helmholtz energy (for example, see Donohue and Prausnitz, 1978), but Equation 7 should be replaced by

$$\epsilon_{ij} = \sqrt{\epsilon_{ii}\epsilon_{jj}} \quad . \quad (10)$$

Corrections to Equations 9 and 10 are usually introduced in the form

$$\epsilon_{ij} = \sqrt{\epsilon_{ii}\epsilon_{jj}} (1 - k_{ij}) \quad (11)$$

$$\sigma_{ij} = (\sigma_{ii} + \sigma_{jj}) (1 - l_{ij})/2 \quad . \quad (12)$$

Binary parameters  $k_{ij}$  and  $l_{ij}$  correct for errors in the mixing rules caused by oversimplifications such as assumptions of similar, spherical intermolecular potentials for all molecules and pairwise additivity. Often Equation 9 is found to be a much better assumption than Equation 10, and the value of  $l_{ij}$  is set to zero. Equations 5, 6, 11, and 12 compose the best set of one-fluid mixing rules in use today.

The one-fluid hypothesis is based on the assumption of random mixing, i.e., the composition in the neighborhood of any given molecule is assumed equal to the bulk composition. This assumption is evident in Equations 5 and 6, where the molecular parameters are averaged according to the product of their mole fractions, this product being proportional to the



probability of choosing two given molecules at random from the mixture.

#### NONRANDOMNESS THEORIES

Although random-mixing theories (such as the one-fluid theory) correlate reasonably well the phase equilibria of simple nonpolar mixtures, they can not accurately predict such equilibria for so-called asymmetric mixtures, i.e., mixtures of molecules that differ greatly in size, shape, or intermolecular potential.

Several approaches to this nonrandomness problem have been taken. One approach is to use the perturbation theory for fluids, first suggested by Zwanzig (1954) and developed by Barker and Henderson (1976) and others. In perturbation theory, the Helmholtz energy is expanded in a reciprocal-temperature power series. The nonrandomness of a mixture enters explicitly into the terms of this series (for example, see Henderson, 1974). Unfortunately, only the first two perturbation terms can be calculated (at the present state of the art for statistical mechanics), and, because the first perturbation term is merely the mean-field term, usually only the first-order corrections for nonrandomness are included in this approach. (See Donohue and Prausnitz, 1978, however, for approximations for higher-order terms.)

Another approach is to consider a chemical-equilibrium hypothesis (chemical theory). By assuming that polar species can form dimers and by fitting data to determine a standard-

state enthalpy and entropy of such a dimerization, Gmehling, Liu, and Prausnitz (1978) have correlated well vapor-liquid equilibria for several polar mixtures.

The chemical theory has three important disadvantages. First, this theory assumes the existence of polymeric species of the polar components. Except in very rare cases (see, e.g., Prausnitz, 1969), this assumption is not realistic; thus, this theory postulates pseudo-components. Second, the chemical theory requires significantly more extensive calculation than, for instance, the one-fluid theory because it requires the solution of chemical- as well as phase-equilibrium equations. As more polar species are added to a multicomponent mixture, the geometric increase in the number of pseudo-components lengthens the required calculations to an intolerable degree. Third, the number of pure-component and binary parameters increases because standard-state enthalpies and entropies of dimerization are required.

We have here chosen the local-composition approach (Whiting and Prausnitz, 1980). This model for nonrandomness dates from 1935, when Guggenheim (1935 and 1952) introduced his quasi-chemical theory. It was put to engineering use by Wilson (1964) and improved and extended to produce the NRTL (Renon and Prausnitz, 1968) and UNIQUAC (Abrams and Prausnitz, 1975) models for liquid-state activity coefficients. The two-liquid theory, which is commonly used to derive these models (cf., Maurer and Prausnitz, 1978; Kemény and Rasmussen, 1981) and which we use here, was developed by Scott (1956).

Only one previous study (Vidal, 1978; Huron and Vidal, 1979) has been made in which the local-composition model, which has proved so successful in correlating liquid-state activity coefficients, has been used in an equation-of-state treatment. Some problems, however, are evident in this treatment by Vidal: (1) the low-density limit (quadratic mole-fraction dependence of the second virial coefficient) is not met, (2) new empirical binary parameters are introduced even though they should be calculable from the intermolecular-potential parameters, and (3) the standard state is not consistent throughout Vidal's derivation. Although he recognizes the utility of existing liquid-state models for equations of state, Vidal makes the unfortunate assumption that the same mixing rules apply for all densities. The model introduced in the next section avoids these problems.

#### LOCAL-COMPOSITION MODEL

We assume that gross nonrandomness occurs even in mixtures of nearly equal-sized molecules if their intermolecular potentials are vastly different. Further, we assume that this nonrandomness exists, to some extent, at all non-zero densities.

First, we separate the Helmholtz energy into a repulsive (hard-sphere) and an attractive part:

$$A = A^{\text{id}} + A^{\text{rep}} + A^{\text{attr}} \quad (13)$$

(See Appendix A for a discussion of how this separation is

made.)

For molecules of nearly equal size, the repulsive Helmholtz energy is calculated with the one-fluid model (Equations 6 and 9) because the unperturbed state (the hard-sphere fluid) is assumed random, i.e., all nonrandomness is caused by the attractive forces.

For a binary mixture, we consider two representative regions in the fluid (see Figure 1). One region centers around a type-1 molecule, and the other centers around a type-2 molecule. The local compositions in these two types of regions are different. As suggested by quasi-chemical theory, we approximate these local compositions using Boltzmann factors with energies characteristic of the like and unlike two-body interactions:

$$\frac{x_{ji}}{x_{ii}} = \frac{x_j}{x_i} \frac{\exp(-\alpha u_{ji}/RT)}{\exp(-\alpha u_{ii}/RT)} \quad (14)$$

$$x_{ji} + x_{ii} = 1 \quad , \quad (15)$$

where  $i=1$  or  $2$  and  $\alpha$  is a binary parameter characteristic of the degree of nonrandomness. (If  $\alpha=0$ , the fluid is random.) Equation 14 indicates that the local composition of  $i$  molecules around a  $j$  molecule is proportional to the total number of  $i$  molecules (required to satisfy the mass balance) and proportional to the Boltzmann factor of an energy,  $u_{ij}$ , characteristic of the attractive  $ij$  interaction. In previous models, this energy was taken to be  $zw/2$ , where  $z$  is the coordination number and  $w$  is the energy between two nearest-neighbor molecules. For liquids, this lattice-theory

simplification may be reasonable, but, for lower densities, we know that  $z$  and  $w$  are functions of temperature and density. For any equation of state of the van der Waals type, we can calculate this characteristic energy as a function of density and temperature--it is merely the attractive internal energy of a system of molecules interacting with an  $ij$ -type intermolecular potential.

The total attractive internal energy of the fluid mixture is the sum of all contributions from the individual molecules:

$$U^{\text{attr}} = N_1(x_{21}u_{21} + x_{11}u_{11}) + N_2(x_{12}u_{12} + x_{22}u_{22}) \quad (16)$$

Equation 16 can be integrated to calculate the attractive Helmholtz energy of the mixture and, then, differentiated to produce a mixture equation of state. This procedure is demonstrated below for the van der Waals equation, but it can be applied to any equation of state for which the repulsive and attractive contributions to the Helmholtz energy can be determined.

#### EXAMPLE. van der Waals Equation

The simplest reasonable equation of state for fluids is the van der Waals (1873) equation,

$$P = \rho RT + \rho^2 bRT/(1-b\rho) - a\rho^2, \quad (17)$$

which we use here for heuristic reasons. By integrating the equation of state over the density, one can obtain an expression for the Helmholtz energy:

$$A - A(T, \rho=0) = N \int_0^\rho \frac{P}{\rho^2} d\rho = A^{\text{id}} + A^{\text{rep}} + A^{\text{attr}}, \quad (18)$$

where

$$A^{\text{rep}} = -NRT \ln(1 - b\rho) \quad (19)$$

$$A^{\text{attr}} = -N a \rho \quad (20)$$

To obtain the attractive part of the internal energy, we use the Gibbs-Helmholtz relation,

$$[\partial (A/T) / \partial (1/T)]_{N,V} = U \quad (21)$$

on the attractive Helmholtz energy:

$$U^{\text{attr}} = \partial (-N a \rho / T) / \partial (1/T) = -N a \rho \quad (22)$$

Equation 14, thus, becomes

$$\frac{x_{ji}}{x_{ii}} = \frac{x_j}{x_i} \exp \left[ \frac{\alpha (a_{ji} - a_{ii}) \rho}{RT} \right] \quad (23)$$

Equation 23 shows an important feature of the local-composition model: the local compositions become identical to the respective bulk compositions at the high-temperature and at the low-density limit. Any consistent treatment of non-randomness must meet these boundary conditions. Furthermore, any equation of state for which the attractive internal energy is proportional to the density in the low-density limit can be used with our local-composition treatment to meet these boundary conditions. All reasonable equations of state have such a density dependence.

Combining Equations 15, 16, and 23, we obtain the attractive potential energy of the mixture:

$$\frac{U^{\text{attr}}}{N} = - \sum_{i=1}^2 \sum_{j=1}^2 x_i x_j a_{ji} \rho \frac{\exp \left[ \frac{\alpha (a_{ji} - a_{ii}) \rho}{RT} \right]}{\sum_{k=1}^2 x_k \exp \left[ \frac{\alpha (a_{ji} - a_{ii}) \rho}{RT} \right]} \quad (24)$$

We now integrate Equation 24, using Equation 21, to obtain the attractive Helmholtz energy of the mixture:

$$\frac{A^{\text{attr}}}{N} = - \sum_{i=1}^2 x_i \left\{ a_{ii} \rho + \frac{RT}{\alpha} \ln \sum_{j=1}^2 x_j \exp \left[ \frac{\alpha (a_{ji} - a_{ii}) \rho}{RT} \right] \right\} \quad (25)$$

Equation 25 can be differentiated with respect to mole number to obtain the attractive chemical potential of either component or differentiated with respect to density to obtain the attractive pressure. The latter leads to the following expression for the total pressure of the mixture:

$$P = \rho RT / (1 - b\rho) + P^{\text{attr}} \quad (26)$$

where

$$P^{\text{attr}} = -\rho^2 \sum_{i=1}^2 x_i \left\{ a_{ii} + \frac{\sum_{j=1}^2 x_j (a_{ji} - a_{ii}) \exp \left[ \frac{\alpha (a_{ji} - a_{ii}) \rho}{RT} \right]}{\sum_{j=1}^2 x_j \exp \left[ \frac{\alpha (a_{ji} - a_{ii}) \rho}{RT} \right]} \right\} \quad (27)$$

Equation 27 is the attractive contribution to the mixture equation of state using the local-composition model with the van der Waals equation. To compare this contribution to that of the one-fluid van der Waals model, we define  $a_{\text{mix}}$  (the effective van der Waals  $a$  for the mixture) as

$$a_{\text{mix}} = -P^{\text{attr}} / \rho^2 \quad (28)$$

where  $P^{\text{attr}}$  is given by Equation 27. This quantity,  $a_{\text{mix}}$ , is plotted in Figure 2 as a function of composition for two densities. Notice that  $a_{\text{mix}}$  for the local-composition (two-fluid) model differs from  $a_{\text{mix}}$  for the random-mixing (one-

fluid) model only at the higher density, as expected. Of particular interest is the difference between the slopes of the local-composition and random-mixing curves. These slopes are related to the chemical potentials of the components of the mixture and suggest that phase equilibria predicted with the two theories are greatly different.

#### LOW-DENSITY LIMIT

Every equation of state for a mixture, at low densities, must give a second virial coefficient with a quadratic mole-fraction dependence (Prausnitz, 1969). By differentiating Equation 27, one obtains for the second virial coefficient

$$B = \frac{1}{RT} \left[ \frac{\partial (P/\rho)}{\partial \rho} \right]_{T, x, \rho \rightarrow 0} = \sum_{i=1}^2 \sum_{j=1}^2 x_i x_j \left( b_{ij} - \frac{a_{ij}}{RT} \right). \quad (29)$$

Thus, this low-density limit is met for the local-composition model with the van der Waals equation. Here again, any equation of state for which the attractive internal energy is proportional to the density in the low-density limit can be used with the local-composition model to give the proper limit.

#### HIGH-DENSITY LIMIT

For liquid-like densities, we know that the local-composition model must become identical to the liquid-state activity-coefficient model on which it is based. To compare these models, we must evaluate the excess Gibbs energy of a mixture, which can be calculated from an equation of state by



evaluating the expression

$$g^E = \mu^r - \sum_{i=1}^m x_i \mu_i^{r, \text{pure}} + RT \ln \rho - RT \sum_{i=1}^m x_i \ln \rho_i^{\text{pure}}, \quad (30)$$

where  $\rho$  is the molar density of the mixture at (T,P),  $\rho_i^{\text{pure}}$  is the molar density of pure liquid i at (T,P), and these densities are used to calculate the respective residual chemical potentials from

$$\mu^r = \frac{\partial}{\partial N} \left[ N \int_0^\rho \frac{(P - \rho RT)}{\rho^2} d\rho \right]_{T, V, x} \quad (31)$$

It is important to note that Equation 30 is valid only when the equation of state has a liquid-like density root for all pure components at (T,P); otherwise, the excess Gibbs energy of the mixture is undefined. If Equation 26 is used in Equation 31, the following infinite-pressure limit for molecules of equal size is obtained:

$$\frac{g^E}{RT} = - \frac{1}{\alpha} \sum_{i=1}^2 x_i \ln \sum_{j=1}^2 x_j \exp \left[ \frac{\alpha (a_{ji} - a_{ii})}{bRT} \right] . \quad (32)$$

Equation 32 is of the same form as the three-parameter Wilson (1964) equation for mixtures of components with equal molar volumes, where

$$g_{ij} - g_{ii} = -(a_{ji} - a_{ii})/b \quad (33)$$

$$c = 1/\alpha . \quad (34)$$

EXTENSION TO MULTICOMPONENT MIXTURES OF LARGE AND SMALL MOLECULES

We extend the local-composition model to multicomponent mixtures by considering  $m$  different types of regions in the fluid, where  $m$  is the number of components. Each type of region contains a molecule of type  $i$  at its center.

To extend our model to mixtures of large and small molecules, we assume that each molecule has an external surface area equal to  $Q_i$ ; only this area is available for intermolecular attraction. If we designate the average attraction per unit surface area of an  $ij$  interaction as  $e_{ij}$  the attractive energy of a type  $i$  region is

$$U^{(i)} = \sum_{j=1}^m x_{ji} q_i e_{ji} \quad , \quad (35)$$

where  $x_{ji}$  is the local composition of type  $j$  molecules in a type  $i$  region.

To calculate the local compositions, we use Equations 14 and 15 with the new definition of  $u_{ji}$  in terms of the surface areas:

$$\frac{x_{ji}}{x_{ii}} = \frac{x_j}{x_i} \exp \left[ \frac{-\alpha q_i (e_{ji} - e_{ii})}{RT} \right] \quad (36)$$

$$\sum_{j=1}^m x_{ji} = 1 \quad , \quad \text{for all } i. \quad (37)$$

It is important to note that Equations 35, 36, and 37 are fundamentally different from similar equations used in the derivation of the UNIQUAC equation. Our equations involve local mole fractions; those in UNIQUAC involve local surface fractions. If local surface fractions had been used here, the

low-density limit would not have been met. Another consequence of our approach is that our model does not reduce to the UNIQUAC model at liquid densities.

To calculate thermodynamic properties, we again sum the contributions to the attractive internal energy of all the regions:

$$\frac{U^{attr}}{N} = \sum_{i=1}^m x_i U^{(i)} \quad (38)$$

Substituting Equations 35, 36, and 37 into Equation 38, we obtain

$$\frac{U^{attr}}{N} = \sum_{i=1}^m \sum_{j=1}^m x_i x_j q_i e_{ji} \frac{\exp\left[\frac{-\alpha q_i (e_{ji} - e_{ii})}{RT}\right]}{\sum_{k=1}^m x_k \exp\left[\frac{-\alpha q_i (e_{ji} - e_{ii})}{RT}\right]} \quad (39)$$

For the simple van der Waals attractive term, the internal energy for pure  $i$  is

$$q_i e_{ii} = a_{ii} \rho \quad (40)$$

If we use the geometric mean for the attractive potential energy of an  $ij$ (segmental) interaction,

$$e_{ij} = \sqrt{e_{ii} e_{jj}} (1 - k_{ij}) \quad (41)$$

the attractive contribution to the pressure for a mixture of van der Waals molecules is

$$p^{attr} = \rho^2 \sum_{i=1}^m x_i \left\{ a_{ii} + \frac{\sum_{j=1}^m x_j (a_{ji} - a_{ii}) \exp\left[\frac{\alpha (a_{ji} - a_{ii}) \rho}{RT}\right]}{\sum_{j=1}^m x_j \exp\left[\frac{\alpha (a_{ji} - a_{ii}) \rho}{RT}\right]} \right\} \quad (42)$$

where

$$a_{ji} = q_i \sqrt{\frac{a_{jj}a_{ii}}{q_i q_j}} (1 - k_{ji}) \quad (43)$$

#### PREDICTION OF VAPOR-LIQUID EQUILIBRIA FOR AQUEOUS SYSTEMS

To show the effect of the local-composition model on calculated phase equilibria, we have applied our model to the systems methane/water and ethane/water. We have chosen a very simple equation of state for our example--the repulsive part is given by the expression of Carnahan and Starling (1969), and the attractive part is given by the van der Waals term:

$$P = \rho RT \left[ \frac{1 + \xi + \xi^2 - \xi^3}{(1 - \xi)^3} \right] - a \rho^2 \quad (44)$$

where

$$\xi \equiv b\rho/4 \quad (45)$$

To determine the values of the pure-component parameters for water, we used the vapor pressure and the density of the saturated liquid at the temperature of interest (Bain, 1964). For the hydrocarbons (which are supercritical at the temperatures considered), we used the fugacity and the density at the desired temperature and at a high pressure (40 MPa) (Angus et al., 1978; Goodwin et al., 1976). From the two data for each component, the parameters  $a$  and  $b$  were determined uniquely.

The binary interaction parameter  $k_{ij}$  was determined from cross-second-virial-coefficient data (Rigby and Prausnitz, 1968, and Coan and King, 1971) for each binary pair. In the

low-density limit, both the random-mixing and the local-composition models give the same second virial coefficient; therefore, we use the same value for  $k_{ij}$  with both models.

The results for methane/water at 300°C are shown in Figure 3. Although both models predict the vapor-phase composition reasonably well, the local-composition model predicts the solubility of methane in the liquid phase much better. In Figure 4, a similar plot is shown for methane/water phase equilibria at 150°C. The difference between the random-mixing and local-composition models is even more striking at this temperature. (Note that the scale for the mole fraction methane at low concentrations is logarithmic.) For both of these temperatures, the local-composition calculations are for  $\alpha=1$ . In the quasi-chemical theory of Guggenheim,  $\alpha$  was not a parameter, but rather it was always unity. Thus, the improvement in the fit of the methane/water data by use of the local-composition model is not at the expense of another binary parameter. If we increase the value of  $\alpha$  to approximately 1.1, the solubility of methane in the liquid phase will be fit even at 150°C.

Figure 5 shows the prediction of the phase equilibria of ethane/water at 300°C. Again, the prediction of the vapor-phase composition is nearly the same for the two models. Because of the oversimplified equation of state, however, this fit is not as good as the fit for methane/water. The composition of the liquid phase is improved with the local-composition model, but here we have had to use  $\alpha=0.35$ . When  $\alpha$

is unity, the liquid-phase composition is overcompensated.

#### CONCLUSIONS

The local-composition model can be applied to a broad range of equations of state in current use. This model enables one to incorporate the effects of nonrandomness into simple equations and, thereby, to extend their usefulness to asymmetric mixtures. Only one new parameter is added in our treatment, no pseudo-components are considered, and the complexity of the computations is not as great as with chemical-theory models. Perhaps most important, this model of nonrandomness in fluid mixtures is internally consistent and meets the necessary low- and high-density boundary conditions.

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# NOMENCLATURE

$a$  = energy parameter in the van der Waals equation

$a_{ij}$  = parameter  $a$  for an  $ij$  interaction

$a_{mix}$  = effective van der Waals parameter  $a$  for a mixture

$A$  = total Helmholtz energy

$b$  = size parameter in the van der Waals equation

$b_{ij}$  = parameter  $b$  for an  $ij$  interaction

$B$  = second virial coefficient

$c$  = parameter in the Wilson equation

$e_{ij}$  = attractive potential energy per unit surface area for an  $ij$  interaction

$E$  = total internal energy

$g^E$  = molar excess Gibbs energy

$g_{ij}$  = parameter in the Wilson equation

$k_{ij}$  = energy interaction parameter for the  $ij$  binary

$l_{ij}$  = size interaction parameter for the  $ij$  binary

$m$  = number of components

$N$  = total number moles

$N_i$  = number of moles of component  $i$

$P$  = pressure

$q_i$  = external surface area of an  $i$  molecule

$R$  = ideal-gas constant

$S$  = total entropy

$T$  = absolute temperature

$u_{ij}$  = molar attractive potential energy of  $ij$  interactions

$U$  = total internal energy

$V$  = total volume

$x_i$  = mole fraction of component i

$x_{ij}$  = local composition of i molecules around a j molecule

$\alpha$  = degree-of-randomness parameter

$\epsilon$  = intermolecular-potential minimum

$\epsilon_{ij}$  = parameter  $\epsilon$  for an ij interaction

$\mu$  = chemical potential

$\xi$  = reduced density

$\rho$  = density (N/V)

$\sigma$  = characteristic diameter of a molecule

$\sigma_{ij}$  = parameter  $\sigma$  for an ij interaction

#### Superscripts

attr = attractive

id = ideal-gas

r = residual (i.e., without the ideal-gas part)

rep = repulsive



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APPENDIX A. Separation of Helmholtz energy into repulsive and attractive parts

Most equations of state in use today are of the van der Waals type. These equations can all be split into a repulsive and an attractive part.

Van der Waals used a very crude model for the repulsive part of his equation, but the important characteristics of the repulsive contribution to an equation of state are included. The repulsive part of the intermolecular potential governs the infinite-temperature properties of the fluid, where its structure is determined by the results of collisions between molecules. The impenetrable nature of the hard-sphere potential (the favorite repulsive potential) also creates a singularity in the pressure at a finite density. In most equations of state, the term (or terms) that represents the repulsive contribution can be found by inspection, based on these two properties.

The attractive part of the equation of state is generally taken as the part that is left after subtraction of the ideal-gas and repulsive terms.

A common misconception is that the repulsive part of the equation of state will contain the entropic contributions, the attractive part containing the enthalpic contributions. Thus, one might express the partition of the equation of state as

$$p^{\text{rep}} = T(\partial S/\partial V)_T - \rho RT \quad (\text{A1})$$

$$p^{\text{attr}} = -(\partial E/\partial V)_T \quad (\text{A2})$$

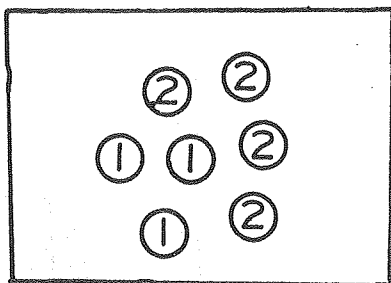
This method will work for the original van der Waals equation, but for many other equations, such as those obtained from perturbation theory, all of the attractive terms except the mean-field term would be considered as part of the repulsive term. A better partition is

$$p^{\text{rep}} = T \left( \frac{\partial P}{\partial T} \right)_{\rho, T \rightarrow \infty} - \rho RT \quad (\text{A3})$$

$$p^{\text{attr}} = p - p^{\text{rep}} - \rho RT \quad (\text{A4})$$

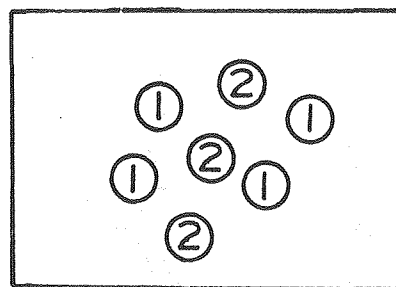
This method will include in the repulsive part only those terms that contain high-temperature entropic contributions.

FIGURE 1. TWO-FLUID THEORY



TYPE-1 REGION

$$U^{(1)} = x_{21}u_{21} + x_{11}u_{11}$$

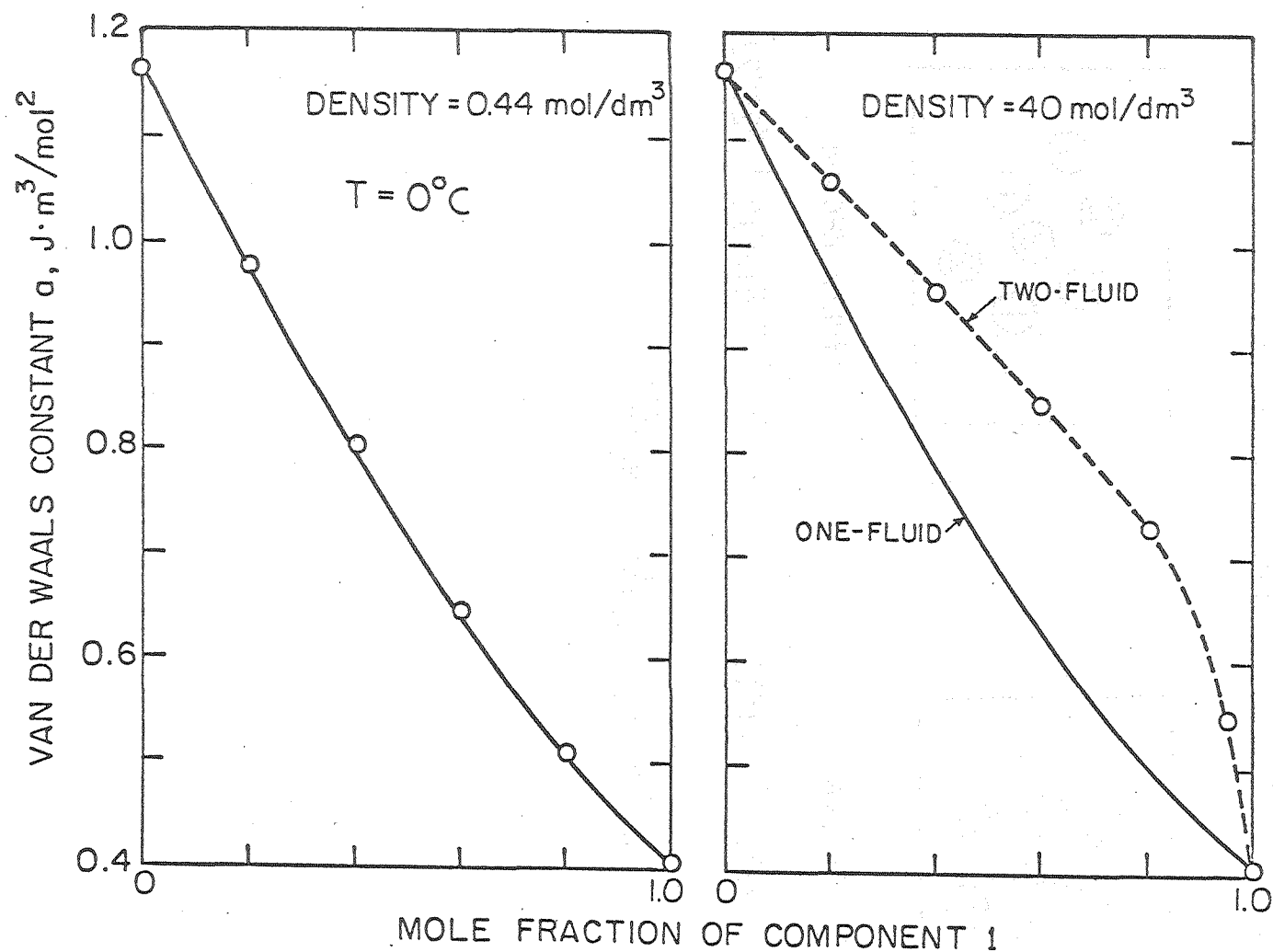


TYPE-2 REGION

$$U^{(2)} = x_{12}u_{12} + x_{22}u_{22}$$

$$U_{ATTR} = N_1 U^{(1)} + N_2 U^{(2)}$$

FIGURE 2.



VAN DER WAALS CONSTANT  $a$  FOR A BINARY MIXTURE, FOR  
ONE-FLUID OR TWO-FLUID THEORY

$$a_{11} = 0.402,$$

$$a_{22} = 1.167,$$

$$a_{12} = 0.634 \text{ J·m}^3/\text{mol}^2$$

FIGURE 3.  
PHASE EQUILIBRIUM FOR METHANE/WATER AT 300°C

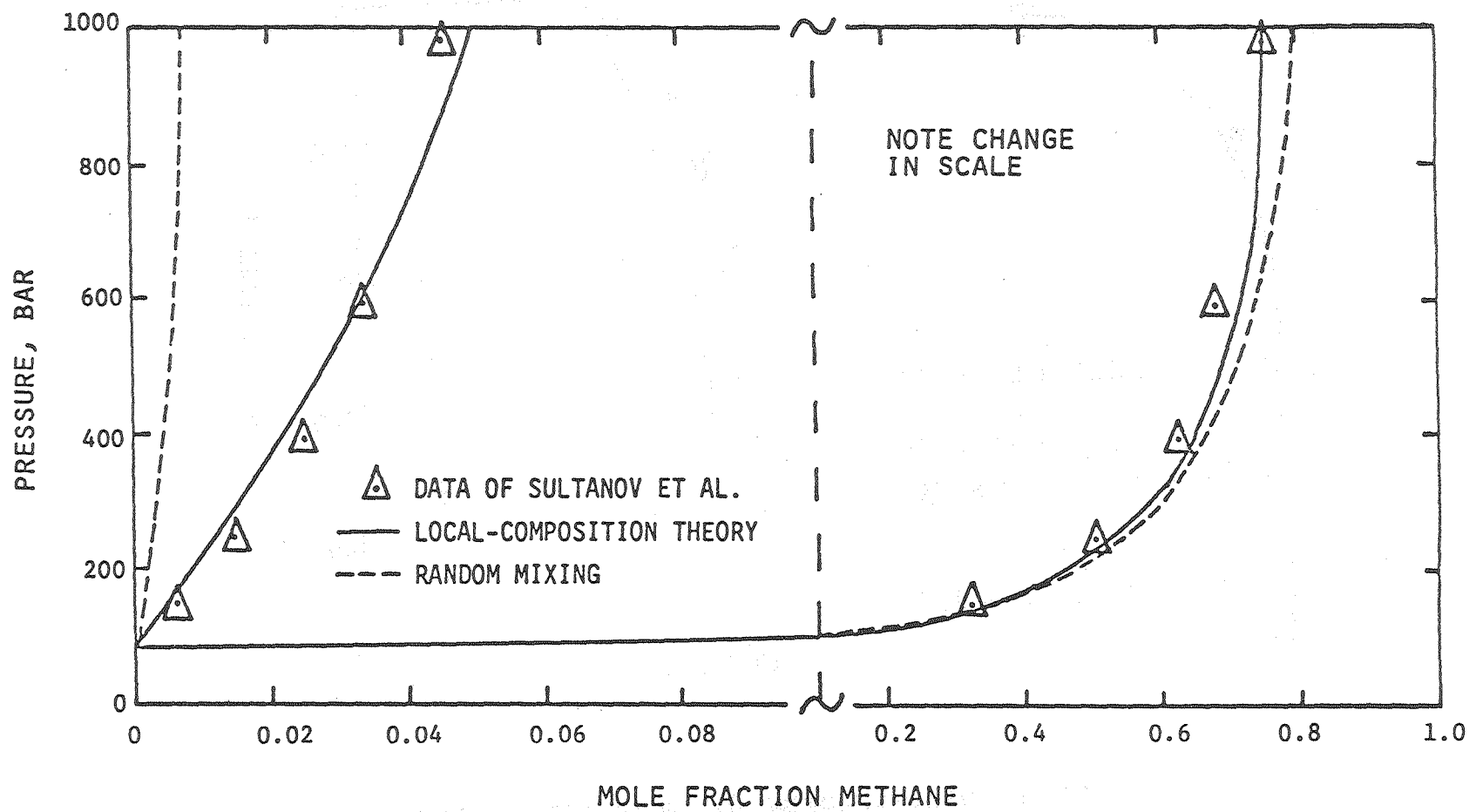


FIGURE 4.  
PHASE EQUILIBRIUM FOR METHANE/WATER AT 150°C

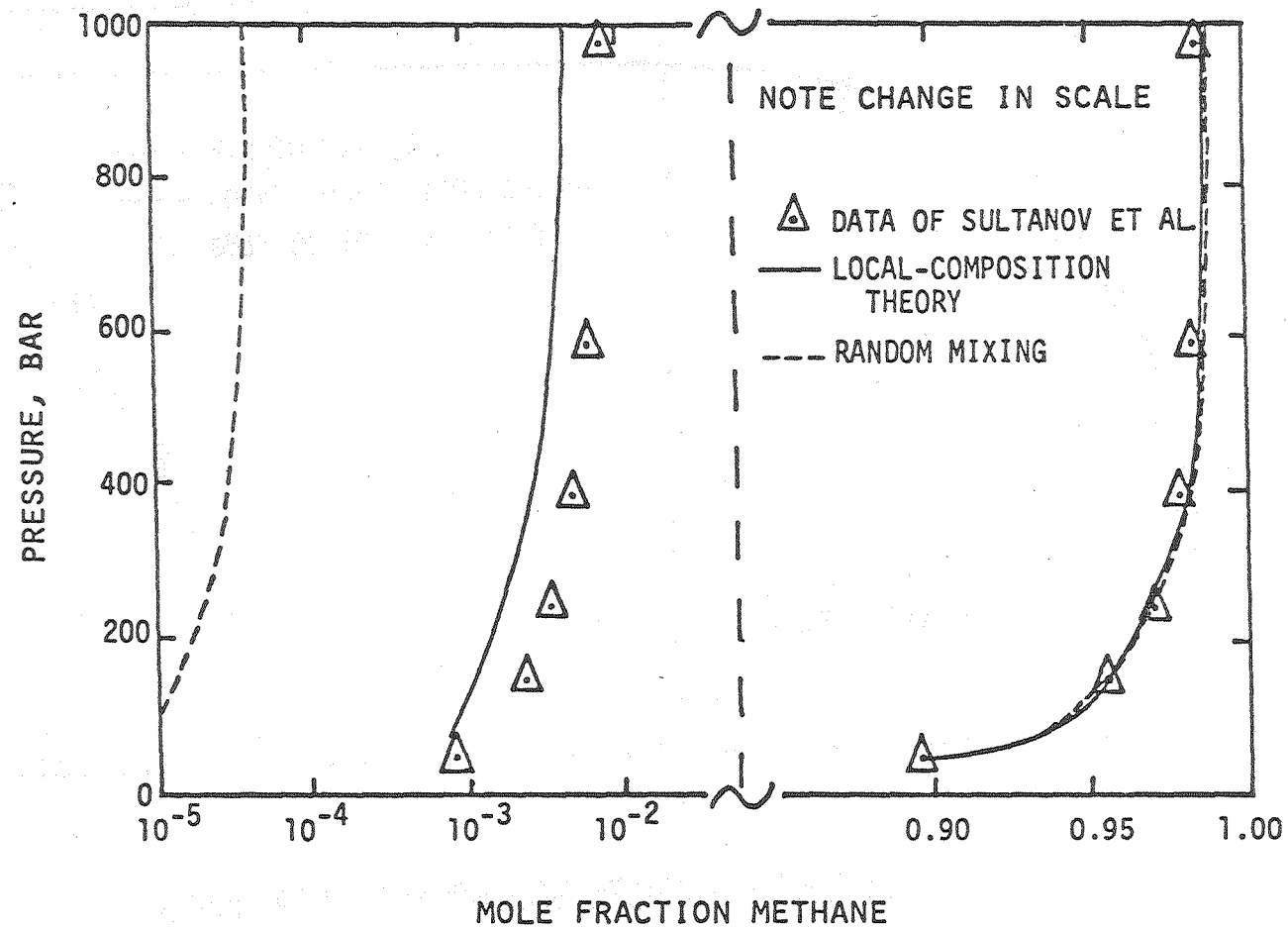




FIGURE 5.  
PHASE EQUILIBRIUM FOR ETHANE/WATER AT 300°C

